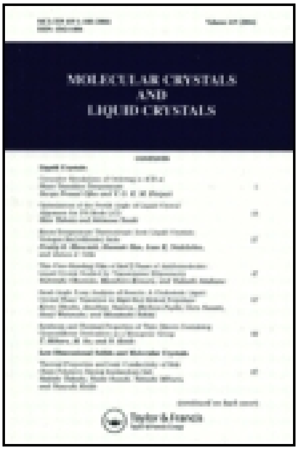

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MORPHOLOGY CONTROL OF LIQUID CRYSTALLINE COMPOSITE GELS BASED ON MOLECULAR SELF-ASSEMBLING KINETICS

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Liquid crystalline composite gels consisting of a low molecular weight gelator and a low molecular weight liquid crystal were prepared by two types of gelation method: (1) a continuous cooling method and (2) an isothermal gelating method, which provide different molecular self-assembling kinetics of

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the low molecular weight gelator in gelation processes. Optical microscopic and atomic force microscopic studies revealed that numerous fine strands of the one-dimensionally assembled low molecular weight gelators were formed in the composite gels in the case of the continuous cooling method as well as that of the isothermal gelating method. However, the thinner strands were more homogeneously dispersed in the composite gel prepared via the isothermal gelation at an appropriate temperature than those of the continuous cooling method. This difference on the dispersion state of the strands was shown, by polarizing optical microscopic observation, to have a significant influence on the molecular alignment state of the low-molecular-weight liquid crystal in the liquid crystalline composite gel. The electro-optical response, the light scattering-transmitting switching, of the liquid crystalline composite gel to an applied electric field was drastically dependent on the morphology of the gelators. High-contrast light switching was achieved for the composite prepared by the isothermal gelation. The response time of the electro-optical switching was less than 100μs under 30 V_{rms}.

Keywords: gel; self-assembling; fibril structure; light scattering; light switching

INTRODUCTION

In recent years, interest in the physical organogel field has increased with the discovery and the synthesis of novel molecules which can gelate organic fluids [1–5]. Noncovalent interactions such as hydrogen bonding, metal coordination, and van der Waals interaction are the main interactions which maintain the gel network in the case of physical organogel. Such molecules typically self-assemble into fibrous aggregates through non-covalent intermolecular interactions in an organic solution, resulting in a self-supporting physical gel in which an organic fluid is embedded in a three-dimensional fibrous network. Gelators derived from isoleucine were found to gelate a wide variety of organic fluids with polar to nonpolar characteristics [6, 7] In this case, the hydrogen bonding between the amide groups played a key role in the organo-gelation. Also, it was reported that liquid crystal molecules were efficiently gelated by the self-assembly of low-molecular-weight gelators through hydrogen bonding [8–10]. On the other hand, (polymer/low-molecular weight liquid crystal) composites have been known since the 1980s to show remarkable light switching between the light-scattering state and the light-transmitting one upon the removal and application of an electric field, respectively [11–20]. The light-scattering and light transmitting states of the (polymer/low-molecular weight liquid crystal) composites are induced by the macroscopically random orientation and unidirectional one of liquid crystal directors embedded in the three-dimensional polymer networks, respectively. Hence the (polymer/low molecular weight liquid crystal) composites have attracted much attention because of their potential for practical applications, such as large-scale displays, switchable windows, and light shutters in projection systems. It is reasonable to suppose that a liquid crystalline gel could show a similar electro-optical effect by analogy from a similarity of the aggregation structure to (polymer/low method weight liquid crystal) composites.

In our previous report [21], a unique hierarchical aggregation structure containing one-dimensional molecular assemblies in micrometer order, fibrous aggregates composed of bundles of numerous one-dimensional molecular assemblies in several 100 nm order and spherulite-like aggregates of grown fibrous aggregates in micrometer order was found in the (low molecular weight gelator/liquid crystal) composite. The spherulite-like aggregates were shown to be responsible for the light switching contrast of an electro-optical effect. Such a morphology of the self-assembling gelators in a liquid crystal must be strongly dependent on the kinetics of the molecular assembly. Only a few attempt have so far been made at morphology control based on molecular assembling kinetics. In this study, two types of gelation processes which result in different molecular assembling kinetics of low molecular weight gelators were investigated for (low molecular weight gelator/liquid crystal) composite systems in order to develop an electrically responsive soft material showing high contrast light switching.

EXPERIMENTAL

Material

The low molecular weight gelator, *N*-bezyloxycarbonyl-L-isoleucylamino-octadecane **1** used in this study was synthesized by us (Kato et al.). The low molecular weight liquid crystal of 4-cyano 4'-pentylbiphenyl **2** (Merck Co. Ltd., Japan) was used without purification. Its chemical structures and some physical properties are shown in Figure 1. The mixture solution of the (**1/2** = 0.5/99.5 mol%) composite in an isotropic state was sandwiched between two indium tin oxide-coated glass plates (10 mm × 20 mm) which were separated by a poly (ethyeleneterephthalate) film spacer of 14 μm thick. No surface treatment for liquid crystal molecular alignment was dome for all the cells.

Preparation of Composite

The (**1/2** = 0.5/99.5 mol%) composite gels were prepared by the two methods as shown in Figure 2. First, in the continuous cooling method, the (**1/2** = 0.5/99.5 mol%) mixture solution was heated up to 373 K, at which

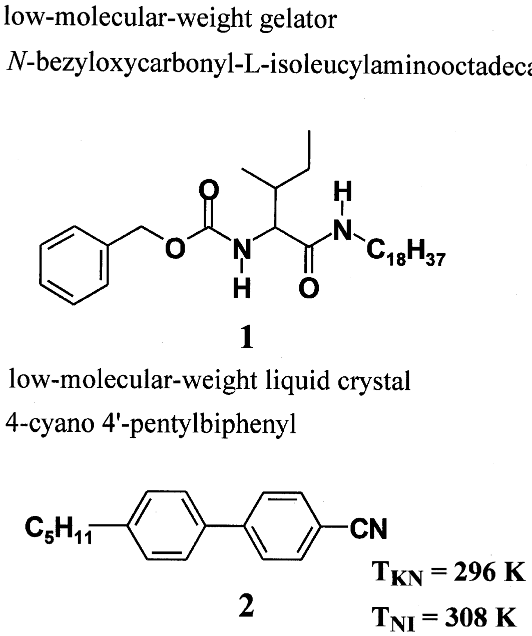

FIGURE 1 Chemical structures and physical properties of **1** and **2**.

point the mixture, in an isotropic sol state, was held for 1.0 h. Then, the mixture solution was continuously cooled to 300 K, at which **2** is in a nematic state at the cooling rate of 1.0 K min^{-1}/. Second, with the isothermal gelating method, the mixture, heated up to 373 K, was held for 1.0 h, followed by cooling it to a certain temperature, T_{gl} slightly below the sol-gel transition temperature of 315 K, and was held for 1.0 h. Then, the mixture was further cooled to 300 K, at which **2** is in a nematic state. The T_{gl} was adjusted with an accuracy of 0.1 K.

Observation of Aggregation Structure

Optical microscopic observation was carried out at 310 K, at which the composite was in an isotropic gel state, in order to evaluate the aggregation structure of the self-assembled low molecular weight gelator. The reason for optical observation at an isotropic gel state is to avoid light scattering from **2** with heterogeneous molecular orientation in a nematic phase. The molecular orientational state of **2** in a nematic phase, that is, the liquid crystalline gel state, was examined by polarizing optical microscopic

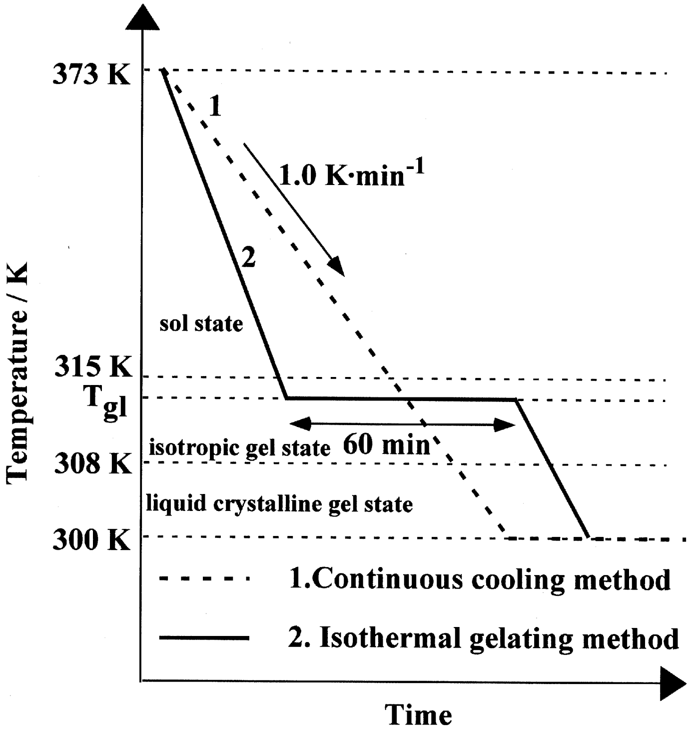

FIGURE 2 Two gelation processes of the composites: continuous cooling method and isothermal gelating method.

observation. The mesoscopic aggregation structure of **1** in the composite gel was observed by atomic force microscopy after **2** was extracted from the composite with *n*-hexane.

Electro-optical Measurements

A He-Ne laser ($\lambda = 632.8$ nm) was used as incident light being transmitted normal to the cell. An external electric voltage from 0 to 40 Vrms was applied across the cell. The transmitted light intensity was measured with a photodiode. The magnitude of the light transmittance of the cell was calibrated by comparing that of the blank cell. The definition of the rise time is the time period required of a change in light transmittance from 10% to 90% upon an electric voltage on-stage. Also, the decay time is a time period required of a 90%–10% transmittance change upon an electric voltage off-state.

RESULTS AND DISCUSSION

Figure 3 shows the optical micrographs for the composite prepared by the continuous cooling (Fig. 3a) and the isothermal gelating at $T_{gl} = 314.5\,K$

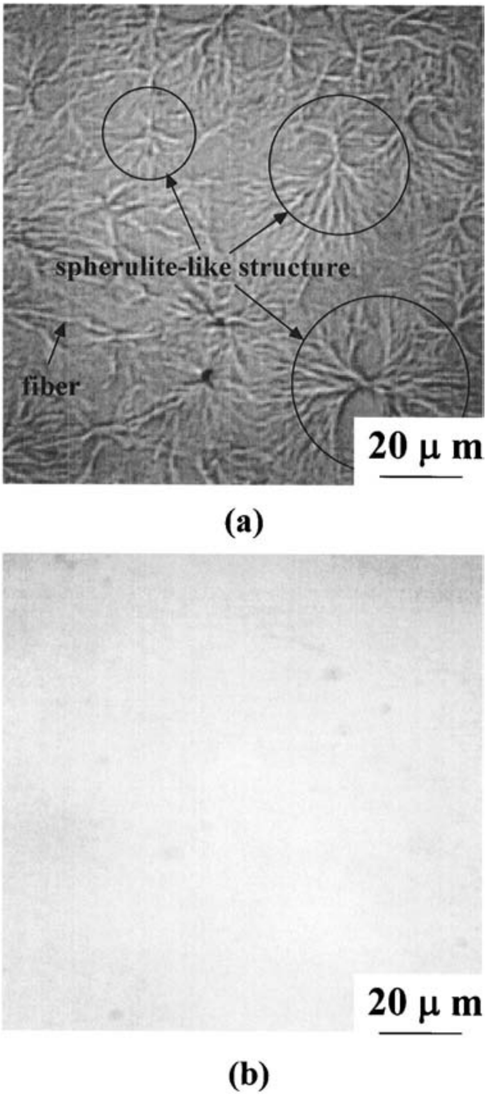

FIGURE 3 Optical micrographs at 310 K for (**1**/**2** = 0.5/99.5 mol%) prepared by (a) continuous cooling method and (b) isothermal gelating method at $T_{gl} = 314.5\,K$.

(Fig. 3b) methods. In the case of the continuous cooling method, a fibrous aggregation texture, including a spherulite-like structure, was formed in the composite, as shown in Figure 3a. The width of the fiber and the diameter of the spherulite-like structure were about 1.0 and 20~30 μm, respectively. It was reported that the (low molecular weight gelator/low molecular weight liquid crystal) composite had a hierarchical structure from the one-dimensional molecular assembly to the higher-order structure such as the spherulite-like aggregation [21]. Therefore, the (**1/2**) composite prepared by the continuous cooling method is likely to form a similar hierarchical structure from the one-dimensional molecular assembly to the spherulite-like aggregation. While, in the case of the isothermal gelating method at $T_{gl} = 314.5\,K$, no morphology was recognized by optical microscopy, that is, no aggregate with a larger dimension than the optical resolution of visible light was present in the composite. This result indicates that the size of molecular aggregation of 1 in the composite prepared by the isothermal gelating method was less than a submicrometer. The optical microscopic observation of Figure 3 conclusively revealed that the difference in the gelation process had a great effect on the higher-order aggregation structure of **1** at an optical size level. The morphology observed by optical microscopy was extremely sensitive to T_{gl}. The $T_{gl} = 314.5\,K$ was a particular temperature of this system because the spherulite-like structure was generated when T_{gl} deviated from 314.5 K even slightly. This means that there is a specific temperature at which generation and growth of a higher-order structure such as the spherulite-like aggregation could be efficiently suppressed. The more detailed mechanism will be discussed later.

Figures 4a and 4b show the AFM images of the composites prepared by the continuous cooling and isothermal gelating methods at $T_{gl} = 314.5\,K$, respectively. Numerous fine strands were observed in the composite prepared by gelation processes. Here, let us refer to the terms “fiber” and “strand,” depending on the width, and “fiber” for μm order and “strand” for nm order (as mentioned later, a fiber is a bundle of many strands). In the case of the continuous cooling method, the width of the strands observed ranged between 180~230 nm, which might correspond to 50~70 molecular assemblies of **1** on the assumption that an extended molecular width of **1** was about 3.5 nm. The width of the bundle was about 1 μm, which was in agreement with the width of the fiber observed by optical microscopy (Fig. 3a). This indicates that the fiber observed in Fig. 3a) was composed of the bundles of many strands. In the case of the isothermal gelating method, finer strands were observed and the width of the strands was between 100~190 nm, which was smaller in comparison to that of the strands in the composite prepared by the continuous cooling method. The width of strands corresponded to that of 30~60

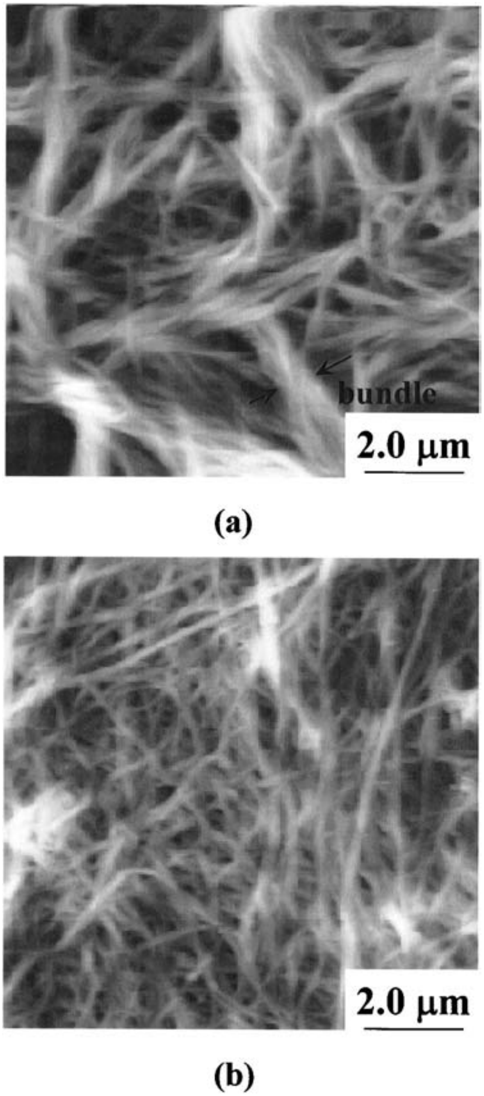

FIGURE 4 AFM images for ($\mathbf{1}/\mathbf{2} = 0.5/99.5$ mol%) after the extraction of **2** with n-hexane: (a) continuous cooling method and (b) isothermal gelating method at $T_{gl} = 314.5$ K.

molecular assemblies of **1**. Also, these fine strands were observed to be homogeneously dispersed in the composite and the number of bundles of fine strands was quite small. Therefore, this result apparently indicates that the isothermal gelating method suppresses the bundling of strands, that is, cohesion among one-dimensional molecular aggregates in the lateral direction.

Figures 5 and 6 show the polarizing optical microscopic observation photographs for the composites prepared by the continuous cooling and

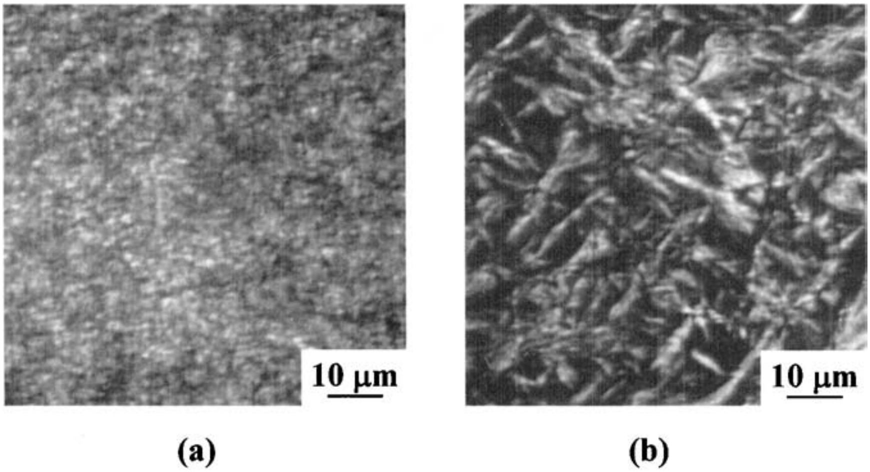

FIGURE 5 (see COLOR PLATES I and II) Polarizing optical micrographs for (**1**/**2** =0.5/99.5 mol%) prepared by continuous cooling method and under (a) 0 and (b) 30 Vrms.

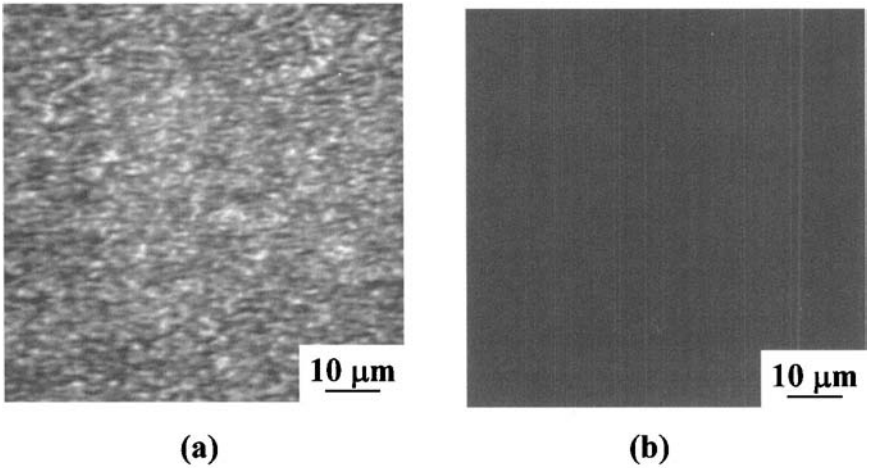

FIGURE 6 (See COLOR PLATES III and IV) Polarizing optical micrographs for (**1**/**2** = 0.5/99.5 mol%) prepared by isothermal gelating method under (a) 0 and (b) 30 Vrms.

isothermal gelating methods at $T_{gl} = 314.5\,K$ upon the application of an electric field of 0 Vrms and 30 Vrms, respectively. As shown in Figures 5a and 6a, a sandy-like texture was observed for each composite without an electric voltage, indicating that liquid crystal media formed polydomains. That is, the alignment of directors of **2** was random in the composite upon the application of an electric field of 0 Vrms. This might be due to the random dispersion of the fibers or strands in the composite. In the case of the application of 30 Vrms, spherulite-like textures were observed in a dark field for the composite prepared by the continuous cooling method as shown in Figure 5b. The dark field region resulted from the realignment of **2** along the direction of the applied electric field, that is, the homeotropic alignment. As reported in our previous article [21], the liquid crystal molecules in the spherulite-like structure of the gelator hardly responded to the applied voltage, but only the dark field texture was observed for the composite prepared by the isothermal gelating method at $T_{gl} = 314.5\,K$ as shown in Figure 6b. This result suggests that the response of **2** to the applied voltage was homogeneous at an optical size level. Figures 5 and 6 reveal that the response of **2** to the applied voltage is strongly related to the aggregation structure of **1** in the composite.

Figure 7 shows a possible gelation method of the composite for the two gelation processes. In the first state of the continuous cooling method as shown in Figure 7 (1), **1** would begin to form the one-dimensional molecular assembly through the hydrogen bonding in a temperature range, which is higher than the sol-gel transition temperature. This molecular assembly was recognized by the result that the intensity of the IR band for the carbonyl group of the amide bond was shifted with a decrease of temperature range from an isotropic sol state to an isotropic gel state [10]. In the second stage, a one-dimensional molecular assembly grows along the bonding axis and also aggregated in the lateral direction with a decrease of temperature, resulting in the formation of strands, as shown in Figure 7 (2). In the further continuous cooling process as shown in Figure 7 (3), the strands aggregate into fibers by bundling in the lateral direction. Depending on the number and position of bundles, a branched structure is created in the fibrous aggregation. As a result, the fiber with a dendritic structure is formed in the composite (Fig. 7 (3)) and then a three-dimensional network of the fibers with a broad distribution of fiber diameters is formed, as shown in Figure 7(4). In the case of the isothermal gelating method at an appropriate temperature (Fig. 7b), the growing of fibrils along the bonding axis seems to be superior to the aggregation of strands in the lateral direction, as shown in Figure 7(5). Therefore, a larger number of fine strands are preferentially formed, as shown in Figure 7(6). As a result, the fine fibers are homogeneously dispersed in the composite.

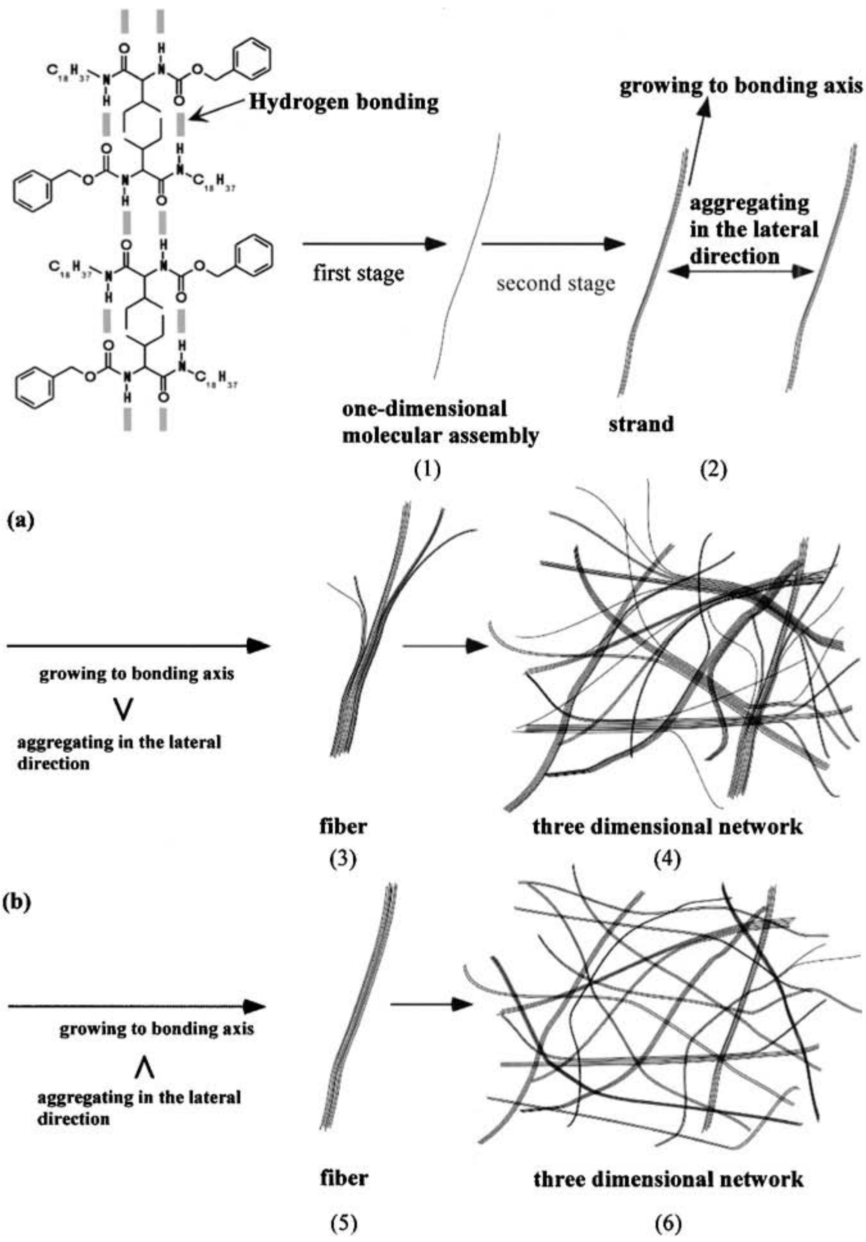

FIGURE 7 A possible model for the gelation of the composite prepared by (a) continuous cooling method and (b) isothermal gelating method at $T_{gl} = 314.5\,K$.

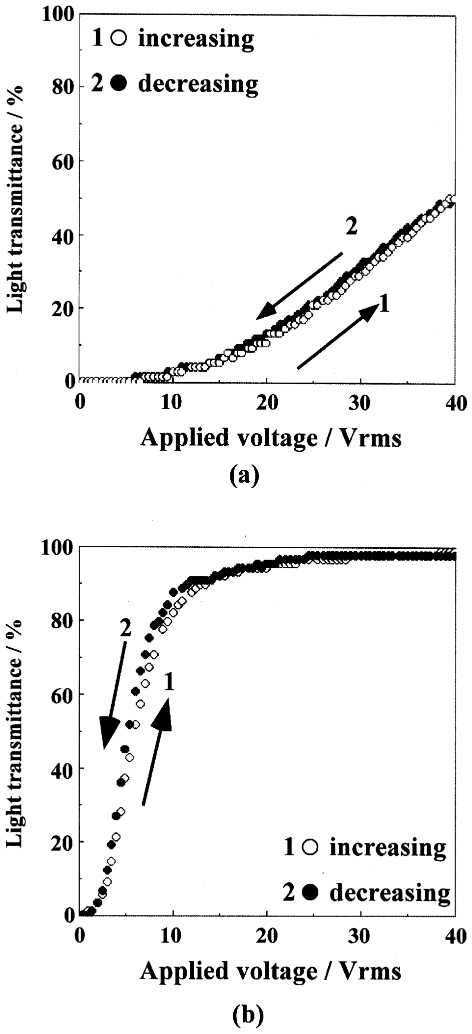

FIGURE 8 Applied voltage dependence of light transmittance for (**1**/**2** = 0.5/99.5 mol%): (a) continuous cooling method, (b) isothermal gelating method at $T_{gl} = 314.5\,K$.

Figure 8a and Figure 8b show the applied voltage dependences of light transmittance for the composites prepared by the continuous cooling method and the isothermal gelating one at $T_{gl} = 314.5\,K$, respectively. Both composites prepared by the two gelation processes exhibited the strong light-scattering state without the application of an electric field. In the case of the continuous cooling method (Fig. 8a), the light scattering might arise from the heterogeneous aggregation structure of fibers or spherulites of **1** as shown in Figures 3a or 4a, and also the ramdom orientation of **2**. Additionally, in the case of the isothermal gelating method (Fig. 8b), the random orientation of **2** might be mainly responsible for the light scattering in the absesnce of an electric field because the fine sandy-like texture in Figure 5a was observed in the composite at 0 Vrms and any heterogeneous

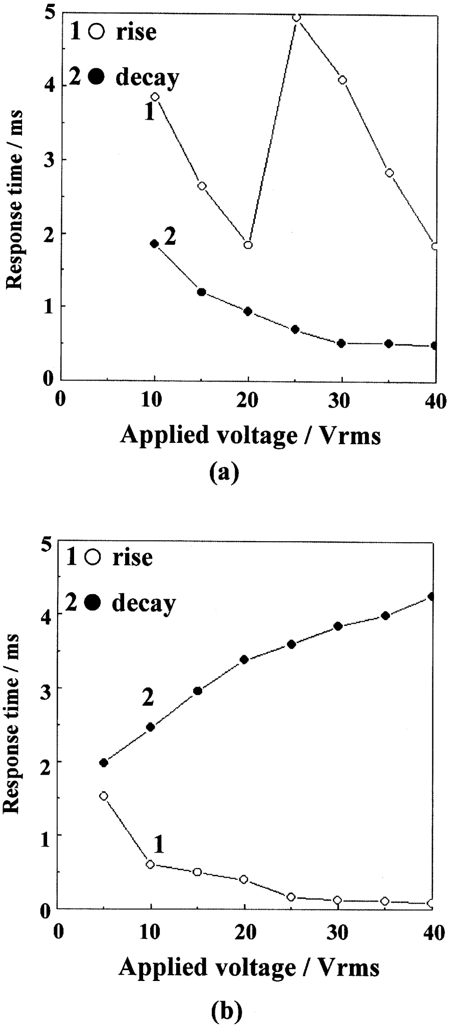

FIGURE 9 Applied voltage dependence of response time for (**1**/**2** = 0.5/99.5 mol%): (a) continuous cooling method, (b) isothermal gelating method at $T_{gl} = 314.5$ K.

aggregation structure such as fibers or spherulite-like structures of **1** with an optical order was not observed in the composite, as shown in Figure 3b. The composite prepared by the continuous cooling method exhibited only 50% of the light transmittance upon the application of an electric voltage of 40 Vrms due to the fairly strong light scattering from the aggregation structure of the gelator with an optical order as shown in Figures 3a and 4a. On the other land, in the case of the isothermal gelating method (Fig. 8b), the composite showed nearly 100% of the light transmittance upon the application of 30 Vrms. These results indicate that a homogeneous dispersion of the fire strands is important to achieve high-contrast light switching between light scattering and transmitting. Moreover, a small hysteresis was observed in increasing and decreasing processes of the applied voltage, as shown in Figure 8b.

Figures 9a and 9b show the applied voltage dependences of response times for the composites prepared by the continuous cooling method and the isothermal gelating one at $T_{gl} = 314.5\,K$, respectively. In the case of the continuous cooling method (Fig. 9a), the rise time was less than 5 ms. The reason for a discontinuous change of the rise time between 20 and 30 Vrms is still unclear at the present time, although the two-step responses of **2** to an applied electric field due to the inhomogeneity of the aggregation structure such as the fiber and the spherulite-like structure **1** in the composite might be attributed to the applied voltage dependence of the rise time. On the other hand, in the case of the isothermal gelating method (Fig. 9b), rise and decay response times less than 5 ms were also attained upon the application of an electric field. The rise time was less than 1 ms under 10 Vrms and, in particular, the rise time was less than 100 μs upon the application of 40 Vrms, as shown in Figure 9b. The fast response of **2** to an applied electric field might be due to the fairly homogeneous dispersion of the domains of **2** in the composite. These results showed that the electro-optical properties of the composite in a liquid crystalline gel state were strongly dependent on the aggregation structure of **1** in the composite, and indicate that the composite with the dispersion of the fine strands of **1** exhibited high-contrast and fast light switching.

CONCLUSIONS

The final morphology of (low molecular weight gelator/low molecular weight liquid crystal) composite systems was sensitively dependent on the gelation process from sol to gel of the low molecular weight gelator dispersed in liquid crystals. Particularly, the formation of aggregation structure at an optical order was depressed and the strands at a mesoscopic order in size were homogeneously distributed in the composite by controlling the gelation process. This result suggests that the kinetics of molecular self-assembling is responsible for the formation of a higher-order aggregation of the gelator. The electro-optical properties of the composite in a liquid crystalline gel state were strongly dependent on the aggregation structure of the low molecular weight gelator in the composite. The high-contrast light switching between light scattering and light transmitting and the fast response to the applied voltage were successfully achieved for the composite prepared by the isothermal gelating method at a proper temperature.

REFERENCES

[1] Terech, P., & Weiss, R. G. (1997). *Chem. Rev.*, *97*, 3133.
[2] Lin, Y., Kachar, B., & Weiss, R. G. (1989). *J. Am. Chem. Soc.*, *111*, 5542.
[3] Brotin, T., Utermöhlen, R., Fages, F., Bouas-Laurent, H., & Desvergne, J. P. (1991). *J. Chem. Soc.*, *Chem. Commun.*, 416.
[4] Hanabusa, K., Tange, J., Taguchi, Y., Koyama, T., & Shirai, H. (1993). *J. Chem. Soc.*, *Chem. Commun.*, 390.
[5] Murata, K., Aoki, M., Suzuki, T., Harada, T., Kawabata, H., Komori, T., Ohseto, F., Ueda, K., & Shinkai, S. (1994). *J. Am. Chem. Soc.*, *116*, 6664.
[6] Hanabusa, K., & Shirai, H. (1998). *Kobunshi Ronbunshu*, *55*, 585.
[7] Hanabusa, K., Tanaka, R., Suzuki, M., Kimura, M., & Shirai, H. (1997). *Adv. Mater.*, *9*, 1095.
[8] Kato, T., Kondo, G., & Hanabusa, K. (1998). *Chem. Lett.*, 193.
[9] Kato, T., Kutsuna, T., Hanabusa, K., & Ukon, M. (1998). *Adv. Mater.*, *10*, 606.
[10] Mizoshita, N., Kutsuna, T., Hanabusa, K., & Kato, T. (1999). *J. Chem. Soc.*, *Chem. Commun.*, 781.
[11] Kajiyama, T., Miyamoto, A., Kikuchi, H., & Morimura, Y. (1989). *Chem. Lett.*, 813.
[12] Miyamoto, A., Kikuchi, H., Morimura, Y., & Kajiyama, T. (1990). *New Polym. Mater.*, *2*, 27.
[13] Miyamoto, A., Kikuchi, H., Kobayashi, S., Morimura, Y., & Kajiyama, T. (1991). *Macromolecules*, *24*, 925.
[14] Kikuchi, H., Usui, F., & Kajiyama, T. (1996). *Polym. J.*, *28*, 35.
[15] Joeng, H. K., Kikuchi, H., & Kajiyama, T. (1996). *Polym. J.*, *20*, 377.
[16] Kajiyama, T., Kikuchi, H., Moritomi, S., & Miyamoto, A. (1989). *Chem. Lett.*, 817.
[17] Kikuchi, H., Moritomi, S., Hwang, J. C., & Kajiyama, T. (1991). *Polym. Advanced Tech.*, *1*, 297.
[18] Yamane, H., Kikuchi, H., & Kajiyama, T. (1997). *Macromolecules*, *30*, 3234.
[19] Kibe, S., Kikuchi, H., & Kajiyama, T. (1996). *Liq. Cryst.*, *21*, 807.
[20] Yang, H., Kikuchi, H., & Kajiyama, T. (2000). *Liq. Cryst.*, *27*, 1695.
[21] Abe, H., Kikuchi, H., Kajiyama, T., Hanabusa, K., & Kato, T. (2002). *Liq. Cryst.*, *29*, 1503.